PREPARATION OF BIODIESEL FROM RBD PALM OIL VIA SINGLE STEP TRANSESTERIFICATION PROCESS WITH THE AID OF ULTRASONIC IRRADIATION AND (NaOH) AS CATALYST

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ABSTRACT

The world is increasingly accepting the fact that conventional sources of fuel and energy are being rapidly depleted and cannot be renewed. One possible alternative to fossil fuel is biodiesel, biodiesel defined as “a substitute for, or an additive to Diesel fuel that is derived from the oils and fats of plants and animals”. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions and its biodegradability. Renewable resources as the raw material for production of biodiesel can be categorized into vegetable oils, animal fat and algae and there are at least four ways in which oils and fats can be converted into biodiesel which are direct use and blending, micro-emulsion, pyrolysis (thermal cracking) and transesterification. Transesterification or alcoholysis is the displacement of alcohol from an ester by another, the presence of a catalyst accelerates the conversion. In this project, the RBD palm oil was used as raw material to produce biodiesel via single step transesterification process in the presence of NaOH as homogeneous alkali catalyst and ultrasonic irradiation. This process was studied in order to find the optimal conditions of the process, the experiment plan was involved three independent variables which are catalyst concentration, reaction temperature and reaction time. The first parameter studied was the catalyst concentrations, the optimal could be achieved at catalyst concentration at 0.5 wt%. The second parameter was the reaction temperature, the optimal temperature is 40°C. The last parameter studied was the reaction time and the result showed that the reaction time at 20 minutes was the best optimal value. Overall, after conducting three different set of experiments, it can be concluded that the best condition for biodiesel production are 71.5% methyl ester with 74.01% product yield and 0.02% moisture contents.

ABSTRAK

Dunia pada hari ini terus menerima kenyataan bahawa punca biasa minyak dan kuasa semakin berkurang dan tidak boleh diperbaharui. Salah satu cara yang mungkin untuk minyak fosil ialah biodisel. Biodisel diertikan sebagai "satu cara menukar, atau satu cara tambahan kepada minyak disel biasa didapati daripada minyak dan lemak dalam tumbuhan dan haiwan". Kelebihan menggunakan minyak cara ini ialah boleh diperbaharui, penyebaran gas yang lebih baik dari ekzos dan ia boleh di biodegrasi. Sumber yang boleh diperbaharui sebagai bahan mentah untuk penghasilan biodisel boleh di kategorikan kepada minyak tumbuhan, lemak haiwan dan alga dan sekurang-kurangnya terdapat empat cara dalam penghasilan biodisel iaitu penggunaan secara terus dan dicampur, makro-emulsi, pirolisis dan transesterifikasi. Transesterifikasi atau pengalkoholan ialah pemindahan dari alkohol daripada ester dengan yang lain, kehadiran pemangkin mempercepatkan penukaran. Dalam projek ini, minyak kelapa sawit digunakan sebagai bahan mentah untuk penghasilan biodisel melalui satu langkah transesterifikasi dengan kehadiran NaOH sebagai pemangkin dan sinaran ultra-sonik. Proses ini dikaji untuk mencari keadaan yang paling bagus untuk tindak balas berlaku, perancangan eksperimen melibatkan tiga pembolehubah iaitu kepekatan pemangkin, suhu tindak balas dan masa tindak balas. Parameter pertama yang dikaji ialah kepekatan pemangkin, keadaan yang paling bagus dicapai pada 0.5 wt%. Parameter kedua yang dikaji ialah suhu tindak balas, keadaan yang paling bagus pada 40°C. Parameter terakhir ialah masa tindak balas dan keadaan yang paling bagus pada 20 minit. Keseluruhannya, selepas melakukan tige set eksperimen yang berbeza, dapat dirumuskan keadaan paling bagus untuk membuat biodisel ialah 71.5% metyl ester dengan 74.01% hasil produk dan 0.02% kandungan kelembapan.

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LIST OF ABBREVIATIONS

RBD	-	Refined, bleached and deoderized
NaOH	-	Sodium hydroxide
FFA	-	Free fatty acid
ASTM	-	American Society for Testing and Material
WCO	-	Waste cooking oil
TLC	-	Thin layer Chromatography

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The world is increasingly accepting the fact that conventional sources of fuel and energy are being rapidly depleted and cannot be renewed. The majority of the world's energy is supplied by petroleum derived fuels and petroleum based distillates are used in a wide range of industrial applications. The oil crisis in the 1970s, depleting reserves, national scarcity issues, price uncertainty and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the extensive use of petroleum in our society. As a result, there has been renewed interest in the discovery of non-petroleum or ‘‘green’’ fuels and chemicals.

Diesel is one of the petroleum-based fuels that have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in agricultural sector. The price of fossil diesel is soaring in these two years and it will be exhausted some day. A lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system such as methanol, ethanol, compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), vegetable oils, reformulated gasoline and reformulated diesel fuel have all been considered as alternative fuels.

1.2 Background of study

One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel. Biodiesel, defined as ‘‘a substitute for, or an additive to Diesel fuel that is derived from the oils and fats of plants and animals’’ or monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. “Bio” represents its renewable and biological source in contrast to traditional petroleum based diesel fuel; “diesel” refers to its use in diesel engines. Biodiesel is the only alternative fuel that runs in any conventional, unmodified diesel engine. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel.

The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and consequently, to the greenhouse effect. One of the disadvantages of using biodiesel is the higher cost of production result from the high price of raw material compare to fossil diesel.

The fast depletion of fossil fuels, coupled with the increasing awareness of environmental issues, concern for increasing green house gas emissions and escalating petroleum prices, have led Malaysia to concerted efforts in the search for renewable and environmentally friendly alternative energy sources. The Malaysian government is refocusing the use of palm oil to the production of biodiesel to cater to the huge demand from European countries, it has encouraged the building of biodiesel plants. Palm oil is a form of edible vegetable oil obtained from the fruit of palm tree. It may have now surpassed soybean oil as the most widely produced vegetable oil in the world. The palm oil obtained from the extraction of the palm fruit. Over the past two decades, Malaysia’s total oil palm planted area increased from 640 000 hectares in 1975 to 4.17 million hectares in 2006. The total oil palm planted area driven mainly in Sabah and Sarawak with a combined growth of 4.5% versus Peninsular Malaysia’s 1.6%. Sabah has the largest oil palm planted area at

1.24 million hectares. Figure 1.1 shows Malaysia's palm oil production by state of total planted area in 2006.

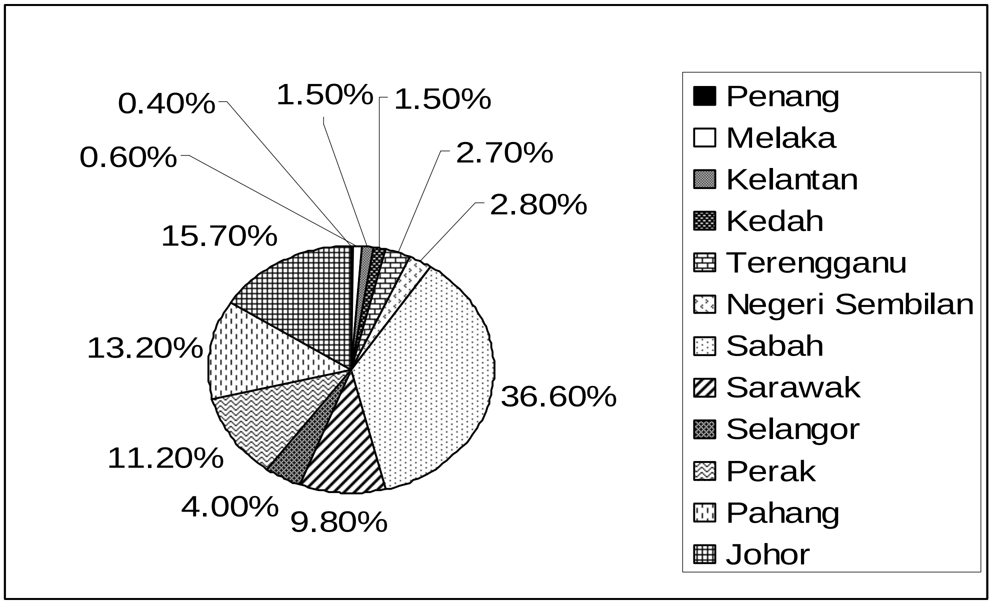

Figure 1.1 Malaysia's palm oil production by state (2006, MPOB)

1.3 Problem statement

Since the announcement of a National Biofuels Policy in August 2005, plantation companies interest in investing in biodiesel production has increased considerably and market growth for this sector is forecast to surpass palm oils traditional market for fats and food processing. The policy not only reduced the green house effect of gas emission from diesel engine but also created new market demand for palm oil industry and can reduced the palm oil's price falling to a low level during excess supply. Malaysia Palm Oil Board (MPOB) has been the pioneer for biodiesel project in Malaysia, several biodiesel companies had run their biodiesel plant such as Golden Hope Plantation Berhad, Malaysia Vegetable Refinery Sdn. Bhd. and Vancee Bioenergy Sdn. Bhd. The interest in this invention from government of Malaysia can be showed by the 75 licenses that had been approved for biodiesel manufactures with total investment of RM 7 billion.

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. Methanol is the most commonly used alcohol because of its low cost and the catalyst used can be varied from acid, alkali or lipase. The used of sodium hydroxide (NaOH) gave some advantages for RBD palm oil because it contained a low amount of free fatty acid (FFA). Only well-refined vegetable oil with less than 0.5% free fatty acid (FFA) can be used as raw material for this alkali transesterification process. The alkali process proved faster and the reaction conditions are moderated.

Due to transesterification process, the mixtures of oil, methanol and catalyst were allowed to react in a reactor. The reactants involve which was methanol and oil was not completely miscible. The present of ultrasonic reactor can reduced the immiscible characteristic of both reactants and increased the mixing efficiency. The mixing efficiency was stated as the main factor affecting the yield of the transesterification process.

1.4 Objective

The aim of this study is to determine the feasibility of single step transesterification process by using homogeneous alkali catalyst, sodium hydroxide (NaOH) with the help of ultrasonic reactor.

1.5 Scope of research work

To achieve the objective of this research, there are three scopes that have been identified:

i. To study the effect of catalyst concentration (NaOH) on the single step transesterification process of RBD palm oil.
ii. To study the effect of reaction temperature on single step transesterification process of RBD palm oil.
iii. To study the effect of reaction time on single step transesterification process of RBD palm oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The majority of the world's energy is supplied by petroleum derived fuels (Brown, 2003; Royal Dutch Shell Group, 1983) and petroleum based distillates are used in a wide range of industrial applications. Petrochemicals serve as raw materials for the chemical industry in the production of solvents, lubricants, paints, and lacquers. The spectacular growth in consumption of crude petroleum during the middle and late twentieth century can be attributed to the ease with which petroleum can be discovered, produced, transported, processed, and utilized (Royal Dutch Shell Group, 1983). The oil crisis in the 1970s, depleting reserves, national scarcity issues, price uncertainty, and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the extensive use of petroleum in our society. As a result, there has been renewed interest in the discovery of non-petroleum or ‘‘green’’ fuels and chemicals.

The price of fossil diesel is soaring in these two years and it will be exhausted some day. A lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system, i.e.: fuel cell, electric power, hydrogen or natural gas for internal combustion engines, etc. One of the promising alternatives that are applied in small scale production is biodiesel. Thus, looking for an alterative way to develop a substitute for Diesel (biodiesel) is an imperious task for humans. Biodiesel, defined as ‘‘a substitute for, or an additive to Diesel fuel that is derived from the oils and fats of plants and animals'' (Ma and Hanna, 1999). The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feed stocks, such as vegetable oil or animal fat. "Bio" represents its renewable and biological source in contrast to traditional petroleum based diesel fuel; "diesel" refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum based diesel. Biodiesel became popular in the markets of developing countries as well as developed ones.

The concept of using of using vegetable oil as fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Dr. Rudolf Diesel invented the diesel engine to run on a host of fuels including coal dust suspended in water, heavy mineral oil, and, vegetable oils. Dr. Rudolf showed his engine at the World Exhibition in Paris in 1900, his engine was running on 100% peanut oil. In 1911 he stated ''the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries, which use it''. Since Dr. Diesel's untimely death in 1913, his engine has been modified to run on the polluting petroleum fuel, now known as ''diesel''. Nevertheless, his ideas on agriculture and his invention provided the foundation for a society fueled with clean, renewable, locally grown fuel (Bryant, 1976).

Biodiesel is the only alternative fuel that runs in any conventional, unmodified diesel engine. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. When biodiesel use alone, it is pure or 100 percent biodiesel fuel and it is necessary to ensure the neat biodiesel fuel meets the biodiesel specification. A biodiesel blend is pure biodiesel blended with petrodiesel. Biodiesel blends are referred to as Bxx. The xx indicates the amount of biodiesel the blend (i.e., a B20 blend is 20 percent biodiesel and 80 percent petrodiesel). It is necessary to make sure the primary criterion for biodiesel quality is adherence to appropriate standard. In the United States, this standard is ASTM D 6751-02 "Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels". Table 2.1 shows the property values required for a mixture of methyl esters to be considered biodiesel. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability. Even in low level blends with conventional diesel fuel, the biodiesel blending stock is expected to meet the standard before being blended.

Table 2.1 : ASTM D 6751–02 Biodiesel Specifications (2002)

Property	ASTM method	Limits	Units
Flash point (closed cup)	D 93	130.0 min	˚C
Water and sediment	D 2709	0.050 max	vol %
Kinematic viscosity, 40˚C	D 445	1.9-6.0	Mm^2/s
Sulfated ash	D 874	0.020 max	mass %
Sulfur	D 5453	0.05 max	mass %
Copper strip corrosion	D 130	N0. 3 max	-
Cetane number	D 613	47 min	-
Cloud point	D 2500	Report	˚C
Carbon residue, 100% sample	D 4530	0.050 max	mass %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020 max	mass %
Total glycerin	D 6584	0.240 max	mass %
Phosphorus content	D 4951	0.001 max	mass %
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D 1160	360 max	˚C

The alternatives to diesel fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available (Srivastava and Prasad, 2000). There are some advantages that justify biodiesel development. It not only provides a market for excess production of vegetable oils and animal fats but also can decreases, although will not eliminate, the country's dependence on imported petroleum. Sheehan *et al*. (1998) stated some advantages on using biodiesel compare to diesel fuel. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel. This fuel is biodegradable and non-toxic. Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment. Barnwal and Sharma (2005) found out the main advantages of using this alternative fuel. It is renewable, better quality of exhaust gas emissions, biodegradable and, given that all the organic carbon present is photosynthetic in origin. So it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy inputs for the biodiesel production are non-fossil-based, and consequently to the greenhouse effect.

Basically oil from renewable feed stock such as vegetable oils and animal fats contain free fatty acids, phospholipids, sterols, water, odourants and other impurities and it cannot be used as fuel directly. Slight chemical modification of the oil is requires to convert it to biodiesel. There are at least four ways in which oils and fats can be converted into biodiesel which are blending, micro-emulsion, pyrolysis and transesterification. Ma and Hanna (1999); Srivastava and Prasad (2000) suggested the best method to produce biodiesel is transesterification. It is the most common method being used in which, oil or fat is reacted with a monohydric alcohol in presence of a catalyst to produce methyl esters. Commonly, biodiesel composed of fatty acid methyl esters that can be prepared from triglyceride which can be founded chemically in oils or fats. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long chain fatty acids, which can be synthesized by transesterification with lower alcohol.

The raw materials for biodiesel production now mainly include biological sources such as vegetable seed oil, soybean oil and some recovered animal fats. Table 2.2 showed physico-chemical properties of biodiesel that were synthesized from some vegetable seed oil and soybean oil. The synthesized biodiesel samples were tested for physico-chemical properties as per ASTM D-6751 and Indian IS-15607 specification.

Table 2.2 : Physico-chemical properties of biodiesel

Property (units)	ASTM 6751 test method	ASTM 6751 limits	IS 15607 test method	IS 15607 limits	Jatropha ME	Pongamia (Karanjia) ME	Sunflower ME	Soybean ME	Palm ME
Flash point (°C)	D-93	Min. 130	IS 1448 P:21	Min. 120	163	141	180	160	135
Viscosity at 40 °C (cSt)	D-445	1.9–6.0	IS 1448 P:25	2.5–6.0	4.40	4.16	4.10	4.00	4.50
Sulphated ash (% mass)	D-874	Max. 0.02	IS 1448 P:4	Max. 0.02	0.002	0.002	0.001	0.001	0.002
Sulphur (% mass)	D-5453	Max. 0.05	ASTM D 5453	Max. 0.005	0.004	0.003	0.003	0.002	0.003
Cloud point (°C)	D-2500	N.A	IS 1448 P:10	N.A	4	4	4	4	16
Copper corrosion	D-130	Max. 3	IS 1448 P:15	Max. 1	1	1	1	1	1
Cetane number	D-613	Min. 47	IS 1448 P:9	Min. 51	57.1	55.1	55.6	58.1	54.6
Water and sediment (vol.%)	D-2709	Max. 0.05	D-2709	Max. 0.05	0.05	0.03	0.04	0.023	0.01
CCR 100% (% mass)	D-4530	Max. 0.05	D-4530	Max. 0.05	<0.01	<0.01	0.01	<0.01	<0.01
Neutralization value (mg, KOH/gm)	D-664	Max. 0.80	IS 1448 P:1/Sec. 1	Max. 0.50	0.48	0.10	0.20	0.15	0.24
Free glycerin (% mass)	D-6584	Max. 0.02	D-6584	Max. 0.02	0.01	0.01	0.02	0.01	0.01
Total glycerin (% mass)	D-6584	Max. 0.24	D-6584	Max. 0.25	0.02	0.01	0.02	0.01	0.01
Phosphorus (% mass)	D-4951	Max. 0.001	D-4951	Max. 0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Distillation temperature	D-1160	90% at 360 °C	Not under spec.	–	90%	90%	90%	90%	90%
Oxidation stability, hrs	N.A	N.A	EN 14112	Min. 6 h	3.23	2.35	1.73	3.80	13.37

2.2 Raw materials

Renewable resources as the raw material for production of biodiesel can be categorized into vegetable oils, animal fat and algae. Ana and Enoch (2003); Han *et al.* (2005) found out that the raw materials for biodiesel production now mainly include biological sources such as vegetable seed oil, soybean oil and some recovered animal fats making it biodegradable and nontoxic and clean renewable fuel with properties similar to conventional diesel.

2.2.1 Animal fats

Ana and Enoch (2003); Han *et al.* (2005) found out some recovered animal fats is one of the raw material for biodiesel production. About 100,000 tonnes of beef tallow is produced annually in Ireland. Much of the lower-grade tallow has been used in animal feed compounds. Legislation to ban the use in animal feeds of tallow from brain and spinal offals is to take effect throughout the EU in 1998, and will generate a supply of tallow for which there is no existing market. In addition, a reduced demand for tallow in animal feeds has reduced its price and increased its attractiveness as a biodiesel feedstock. Preliminary laboratory tests at Oak Park suggest that a good quality biodiesel could be produced from tallow, but more work needed to establish process requirements and methyl ester properties.

2.2.2 Vegetable oils

Vegetable oils can be divided into two categories, virgin oil and waste cooking oil (WCO). Shay (1993) proved the use of vegetable oils as alternative fuels. It has been around for 100 years when the inventor of the diesel engine Rudolph Diesel (1900) first tested peanut oil, in his compression ignition engine. The fuel properties of vegetable oils used in the production of biodiesel was expected o meet the standard of biodiesel specification before being used. Table 2.3 showed some fuel properties of some vegetable oils that used in biodiesel production.

Table 2.3 : Fuel properties of the vegetable oils (Fukuda *et al*., 2001)

Vegetable oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	—	176	0.883	33.6
Soya bean	4.5	45	1	−7	178	0.885	33.5
Babassu	3.6	63	4	—	127	0.875	31.8
Palm	5.7	62	13	—	164	0.880	33.5
Sunflower	4.6	49	1	—	183	0.860	33.5
Tallow	—	—	12	9	96	—	—
Diesel	3.06	50	—	−16	76	0.855	43.8
20% biodiesel blend	3.2	51	—	−16	128	0.859	43.2

2.2.2.1 Virgin oil

The virgin oil mostly used to produce biodiesel was prepared from edible oils such as peanut, soybean, palm, sunflower and corn. These oils are essentially edible in nature. Kaul *et al.* (2003) mentioned that a few attempts have been made for producing biodiesel with non-edible oils like karanja and jatropha, especially in India to reduce the cost of raw material. Non-edible oils such as mahua, karanja, babassu, jatropha and neem are easily available in many parts of the world and are cheaper compound. Busson-Breysse *et al.* (1994) have been carefully analysed the existent of jojoba oil-wax as one of the raw materials in producing biodiesel. Jojoba oil-wax contains minor amounts of free fattyacids and alcohols, phytosterols, tocopherols, phospholipids and trace amounts of a triacylglycerol.

The advantage of using virgin oils is it contains low percent of free fatty acid (FFA). Free fatty acid will deduct the conversion efficiency when alkali catalyst used. Several researches found that the free fatty acid (FFA) neutralisation can be avoided by using refined vegetable oils (Wright *et al*., 1944; Bradshaw and Meuly, 1944; Feuge and Gros, 1949; Freedman *et al.*, 1984). Table 2.4 shows detailed fatty acid composition of different vegetable oils that used as the raw material in biodiesel production.

Table 2.4 : Fatty acid composition of vegetable oil (Srivastava and Prasad, 2000)

Vegetable oil	Fatty acid composition (wt%)									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0
Rice-bran	0.4–0.6	11.7–16.5	1.7–2.5	0.4–0.6	–	0.4–0.9	39.2–43.7	–	26.4–35.1	–
Sal	–	4.5–8.6	34.2–44.8	6.3–12.2	–	–	34.2–44.8	–	2.7	
Mahua	–	16.0–28.2	20.0–25.1	0.0–3.3	–	–	41.0–51.0	–	8.9–13.7	–
Neem	0.2–0.26	13.6–16.2	14.4–24.1	0.8–3.4	–	–	49.1–61.9	–	2.3–15.8	–
Karanja	–	3.7–7.9	2.4–8.9	–		1.1–3.5	44.5–71.3	–	10.8–18.3	–

Tr: Traces.

2.2.2.2 Waste cooking oil (WCO)

The small-scale plant for production of biodiesel from waste coking oil (WCO) has been established in Austria for several years (Mittelbach, 1996). Krawczyk (1996); Connemann and Fischer (1998) reported that approximately 70–95% of the total biodiesel production cost arises from the cost of raw material that is, vegetable oil or animal fats. Therefore, the use of waste cooking oil should greatly reduce the cost of biodiesel because waste oil is available at a relatively low price.

Many researchers found that biodiesel can be produced from waste oils such as used frying oil (UFO) (Supple *et al.*, 2002; Mohamad and Al-Shoukh, 2002; Gonzalez Gomez *et al.*, 2002; Leung, 2001; Guo and Leung, 2003). Nowadays, most of the used cooking oil is poured into the sewer system of the cities. This practice contributes to the pollution of rivers, lakes, seas and underground water, which is very harmful for environment and human health (Hamasaki *et al.,* 2001; Wilsee, 1998). In China, the waste cooking oil was collected by environmental protection agency authorized by local government to prevent the environment pollution. It is estimated that the WCO collected in Guangzhou, the third biggest city in China, is over 20 000 t each year. This collected material is a good commercial choice to produce biodiesel due to its low cost. One of the disadvantages of using waste cooking oil (WCO) was they possessed a much higher acid value than the neat oil indicating the presence of a large amount of free fatty acid (FFA) in the waste oils that could not be converted to biodiesel using an alkaline catalyst.

2.3. Process

There are at least four ways in which oils and fats can be converted into biodiesel which are direct use and blending, micro-emulsion, pyrolysis (thermal cracking) and transesterification. Among these, the transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils.

2.3.1 Direct use and blending

Vegetable oils can be directly use or blends with fossil diesel. Ma and Hanna (1999) stated that in Brazil, Caterpillar (1980) used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% mineral diesel was successful. Some short-term experiments used up to a 50/50 ratio. Pramanik *et al.* (2003) found that 50% blend of Jatropha oil can be used in diesel engine without any major operational difficulties but further study is required for the long-term